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(72) Inventor: Takeshi FUJITA

2-21-13 Urakamidai, Yokosuka-shi, Japan

(72) Inventor: Michio FUKATSU

1-8-12 Jiandai, Kanazawa-ku, Yokohama-shi, Japan

(72) Inventor: Junsuke YAGI

63-6 Minamihonjukucho, Asahi-ku, Yokohama-shi, Japan

(72) Inventor: Kiyonobu NIWA

1-17-13 Tenya, Tsurumi-ku, Yokohama-shi, Japan

(71) Applicant: Nitto Kagaku Kogyo K.K.

5-1 Marunouchi-1-chome, Chiyoda-ku, Tokyo-to, Japan

(74) Agent: Patent Attorney Kiyoshi INOMATA and three others

## SPECIFICATION

### 1. Title of the Invention

A method for the production of methylamines

### 2. Scope of the Patent Claim

1. A method for the production of methylamines in which a mixture comprising (1) freshly provided ammonia and methanol and (2) recovered unreacted ammonia and methanol and also one or more of the methylamines is passed through a flow-through type fixed bed reactor which has been packed with catalyst wherein the reactor exit gas, after undergoing heat exchange with the gas entering the reactor, is utilized in the ways outlined below.

- a) If any of the components of the abovementioned mixture are liquids then it is used as part or all of the heat source when this is being vaporized, and(or)
- b) It is used as part or all of the heat source of the reboiler when a mixture of monomethylamine and dimethylamine obtained from the reactor exit gas is being distilled and the amines are being separated.

2. The method disclosed in claim 1 wherein the catalyst is a zeolite-based catalyst.

3. The method disclosed in claim 1 or claim 2 wherein the material which should be vaporized in the process contains (1) freshly supplied ammonia and methanol and (2) recovered liquid ammonia, methanol and one type or two or more types of methylamine.

4. The method disclosed in any one of claims 1 to 3 wherein the reaction pressure in the reactor is from 5 to 25 kg/cm<sup>2</sup>(G) and the methanol conversion at the reaction stage is from 80 to 95%.

### 3. Detailed Description of the Invention

#### Background of the Invention

The invention concerns improvement of the method for the industrial production of methylamines.

Methylamines can be produced by reacting ammonia and methanol at a high temperature in the vapor phase in the presence of a dehydration catalyst.

The reaction product is a mixture of ammonia, monomethylamine, dimethylamine, trimethylamine, methanol and water. Distillation separation procedures are used to obtain the product methylamines from the reaction product.

A system with a total of four distillation columns is typically used for the distillation separation procedure. That is to say, the reaction product is supplied to a first distillation column and most of the ammonia is removed from the column top and the column bottom material is supplied to a second distillation column. In the second distillation column all of the trimethylamine is removed from the column top by means of a water extraction distillation procedure and the column bottom material is supplied to a third distillation column. In the third distillation column all of the methanol and water are removed from the column bottom and the column top material comprising monomethylamine and dimethylamine is supplied to a fourth distillation column. In the fourth distillation column monomethylamine is recovered from the column top and dimethylamine is recovered from the column bottom.

With this system the monomethylamine is recovered from the column top of the fourth distillation column, dimethylamine is recovered from the column bottom of the fourth distillation column and trimethylamine is recovered from the column top of the second distillation column as the products of the reaction. On the other hand, as well as ammonia, monomethylamine, a small amount of dimethylamine and trimethylamine which has been distilled off azeotropically with these amines are included in the column top material from the first distillation column, and this material is recycled to the reaction system. The column bottom material from the third distillation column is also usually supplied to a separate distillation column and the methanol is recovered from the column top and the recovered methanol is recycled to the reaction system.

Furthermore, there are cases where, because of the product demand for the individual methylamines, some of the monomethylamine and(or) trimethylamine is in excess and these are also recycled to the reaction system.

As indicated above, there are many recycling connections between the reaction system and the refining system in the methylamine production process.

The amounts recycled in each case vary according to the operating conditions of the reaction system, which is to say the temperature, the pressure, the ratio (N/C) of the numbers of atoms of nitrogen and carbon in the mixture which is being passed through the reactor and the type of catalyst which is being used, and they also vary according to the product ratio of the three types of methylamine.

Among the three types of methylamine, the industrial demand at the present time is biased toward dimethylamine. Hence, a high dimethylamine content in the

reaction product, and especially a high proportion of dimethylamine among the three types of methylamine, is desirable.

Now, the catalysts which are being used industrially at the present time are porous silica-alumina based systems which have an average pore diameter of at least 20 Å. When carrying out a reaction using these catalysts the ratio of the three types of methylamine in the reaction product is the equilibrium value which is determined thermodynamically and not much dimethylamine is produced.

From the viewpoint of the thermodynamic equilibrium value, a higher reaction temperature and a higher N/C ratio is useful for producing dimethylamine (but if the reaction temperature is too high then much by-product other than the methylamines is produced and the catalyst life is also shortened). If the N/C ratio is too high then the ammonia and monomethylamine contents of the reaction product are increased and, as a result, the amount of material being recycled is increased and this is not convenient. The pressure has no effect on the thermodynamic equilibrium and this is determined in accordance with the economic aspects of the overall production process.

On the basis of the facts outlined above, the reaction conditions of the production of methylamines which is being used industrially at the present time are as indicated below.

Reaction Temperature = 360 to 440°C

Reaction Pressure: = 15 to 25 kg/cm<sup>2</sup>(G)

N/C = 1.0 to 3.0

Under these conditions the amount of material recycled from the refining system to the reaction system reaches from 3 to 5 times the total amount of ammonia and methanol used as raw materials. This is significant in that a very large amount of energy is required for the separation and extraction of the recycled materials, to raise the pressure to the reaction pressure and to raise the temperature to the reaction temperature.

Catalysts which have a higher selectivity for dimethylamine have been developed more recently with a view to achieving some improvement in this respect. Such catalysts have been suggested by the present inventors (see Japanese Unexamined Patent Applications Laid Open 57-169444, 57-169445, 58-82768 and 58-100949). That is to say, the use and effects of mordenite-based zeolites as catalysts has been suggested. With these catalysts, the one-pass selectivity of

dimethylamine when using a mixture of ammonia and methanol as the raw material is more than two times that obtained with a conventional catalyst, and the catalyst activity is also high and so the reaction can be carried out at a lower temperature of not more than 330°C.

### Outline of the Invention

#### Summary

The invention involves not just the catalyst performance as outlined above for reducing the amount of recycling between the reaction system and the refining system but also involves the operating conditions of the reaction system and the refining system and enables the high overall energy consumption to be reduced and enables the large amount of steam for heating purposes which accounts for a considerable proportion of this energy to be reduced. For this purpose effective use is made of the waste heat energy of the reactor exit gas (the reaction product).

That is to say, in the method for the production of methylamines of the present invention, when producing methylamines by passing a mixture comprising (1) freshly provided ammonia and methanol and (2) recovered unreacted ammonia and methanol and also one or more of the methylamines through a flow-through type fixed bed reactor which has been packed with catalyst, the reactor exit gas, after undergoing heat exchange with the gas entering the reactor, is utilized in the ways outlined below.

- a) If any of the components of the abovementioned mixture are liquids then it is used as part or all of the heat source when this is being vaporized, and(or)
- b) It is used as part or all of the heat source of the reboiler when a mixture of monomethylamine and dimethylamine obtained from the reactor exit gas is distilled and the amines are being separated.

#### Effect

Even with the conventional catalysts, the heat of the reactor exit gas is used for heat exchange with the gas entering the reactor. However, in this case a large quantity of heat is exchanged and the temperature of reaction product after heat exchange is too low and, on the other hand, the liquefaction temperature is too low for utilization of the latent heat of liquefaction which has a high value, and in neither case there much useful the heat, and at the present time the temperature is generally reduced with cooling water and the material sent to the refining system.

In the present invention, the amount of recycling between the reaction system and the refining system is greatly reduced and, moreover, by arranging a heat exchanger for the circulating gas in the reactor the temperature of the product gas which has undergone heat exchange with the gas entering the reactor is raised and the liquefaction temperature of the reaction product is also raised and utilization of the heat contained in the reaction product is simplified. The utilization of this heat involves firstly the vaporization of the methanol and ammonia raw materials (this has accounted for the greatest proportion of steam used for heating in the past) and secondly as a heat source for the reboiler for the distillation and separation of monomethylamine and dimethylamine in the refining system.

### Practical Explanation of the Invention

#### The Production Process

An embodiment of a production process for carrying out the present invention is shown in Figure 1.

In Figure 1, the liquid mixture of ammonia and methanol which is supplied as the raw material is introduced into the evaporator A and vaporized and mixed with the gaseous material being recycled from the refining system and then introduced into the gas/gas heat exchanger B and heated to the reaction starting temperature and introduced into the reactor C which has been packed with a zeolite-based catalyst.

The reactor C has an intermediate heat exchanger C' which is cooled with the circulating gas which is being recycled from the refining system in the middle and the rise in temperature due to the exothermic reaction is suppressed.

The reactor exit gas of which the temperature has been raised by reaction is introduced into the gas/gas heat exchanger B and, after raising the temperature of the gas entering the reactor, it is introduced into the heat exchanger A and forms the heat source for the vaporization of the raw material. The reaction product which emerges from the heat exchanger is conducted to the refining system.

The refining system comprises the distillation column D in which the ammonia is separated off, the distillation column E in which the triethylamine is separated off, the distillation column F in which the methanol and water and dimethylamine are separated off and the distillation column G in which the monomethylamine and dimethylamine are separated.

### The Operating Conditions

The ideal operating conditions for each process and each piece of equipment for making the invention work efficiently are as indicated below.

The distillation column D has at least 30 plates and is operated at a column top pressure of from 12 to 20 kg/cm<sup>2</sup>(G), and ammonia is separated off from the column top. Any monomethylamine above the amount which is required as a product is separated off with the ammonia at this time.

Trimethylamine is also separated off from the column top as an azeotropic mixture with the monomethylamine and ammonia but the remainder, together with the dimethylamine, methanol and water, forms the still material.

It is important here that the amount of triethylamine in the still material should be suppressed to the amount which is required as a product. This is controlled by controlling the operating conditions, and especially the reaction temperature, in the reactor and suppressing the conversion of methanol at the reaction stage. This can be achieved by making use of the fact that the zeolite catalysts enable the production of trimethylamine to be controlled over a wide range by suppressing the conversion of methanol. A methanol conversion can be selected in accordance with the proportion of product trimethylamine which is required, and it is appropriately set within the range of from 80 to 95% of the methanol entering the reactor (less trimethylamine is produced at lower conversion).

Control of the methanol conversion can be carried out by controlling the reaction temperature as mentioned earlier, and if the reaction temperature is low then the methanol conversion is low. Control of the reaction temperature can be carried out easily by a combination of changing the amount of fluid bypassing the gas/gas heat exchanger B and changing the temperature of the gas entering the reactor, and by changing the amount of bypass of the circulating gas from the refining system which is introduced into the intermediate heat exchanger C' in the reactor C. The preferred temperature in this invention is a gas temperature on entering the reactor of from 250 to 290°C and a reactor exit gas temperature of from 300 to 340°C.

In this way the amounts of the three types of methylamine in the column bottom material of the distillation column D are in each case set to the amount which is required as a product and there is no need for subsequent recycling to the reaction

system of excess monomethylamine and trimethylamine which have been separated by distillation as was the case in the past.

The column top gas from the distillation column D is condensed with just the required reflux and the remainder is recycled to the reaction system with compression as it is in the gaseous state. Here, the liquid mixture of ammonia and methanol which is being supplied as raw material is below the boiling point and, with a view to facilitating the evaporation in the evaporator A, the column top gas over the amount which is required for reflux of the distillation column D is condensed and added to the raw material as shown by the broken line in Figure 1 (line 2) and this is an effective procedure for executing the invention effectively.

The distillation column E has at least 40 plates and is operated at a column top pressure of from 4 to 8 kg/cm<sup>2</sup>(G). Here trimethylamine is separated off from the column top as the total amount of that product by extractive distillation with the introduction of water (line 3) close to the column top.

The distillation column F has at least 30 plates and is operated at a column top pressure of from 4 to 7 kg/cm<sup>2</sup>(G). Here the high boiling point materials (methanol, water) other than the methylamines are separated off from the column bottom (line 4).

The distillation column G has at least 40 plates and the column top pressure is preferably as low as possible for utilizing the heat of the reaction product in the reboiler H which is established in the column bottom which is one of the main features of the invention. However, the column top gas is condensed and refluxed and water can be used for this cooling and so there is a limit to the column pressure, and a column top pressure of from 4 to 7 kg/cm<sup>2</sup>(G) is appropriate. Here monomethylamine is separated off from the column top and dimethylamine is separated off from the column bottom, as product in each case.

The reaction product emerging from the evaporator A is partially liquefied, and it is introduced into the reboiler H of distillation column G either as it is or as just the gas phase after gas/liquid separation. Heat is given up again in the reboiler H and the reaction product which has been liquefied further is introduced into an intermediate stage of the distillation column D together with the liquid phase obtained by the abovementioned gas/liquid separation, as required. Then, the intended refinement is achieved by passing through the distillation columns E → F → G.



The column bottom material of distillation column F is sent to a separate distillation column (not shown in the drawing) from the line 4 and there the methanol is recovered and recycled as raw material to the reaction system. At this time waste water with a high temperature of at least 140°C is produced and the heat of this is used to pre-heat the raw materials and the recycled liquid which has been sent from the refining system to the reaction system.

Except for the points outlined above, no limitation is imposed upon the concept of the invention, and the technology which has been used in the known methods for the production of methylamines can be adopted appropriately. For example, a porous solid acid catalyst of average pore diameter at least 20 Å comprising principally silica and(or) alumina as used in the past can be used instead of the zeolite catalyst as a synthesis catalyst in cases where the demand for triethylamine is high. Moreover, one preferred practical example of a zeolite-based catalyst has been disclosed in the aforementioned patent application specification.

#### Illustrative Example

This was carried out using the production process shown in Figure 1. Methanol (2160 kg/h), 540 kg/h of ammonia and part (633 kg/h) of the reflux liquid from distillation column D (comprising 67.2% ammonia, 23.3% monomethylamine, 4.6% dimethylamine and 4.8% trimethylamine (here % signifies wt%, same hereinafter)) was pre-heated with the still material from distillation column F and set to 105°C and then sent to the evaporator A and vaporized by means of the reaction product (via heat exchanger B) and heated to 155°C, mixed with column top gas (2530 kg/h, 215°C) from the distillation column D emerging from the intermediate heat exchanger C' in the reactor and then sent to the gas/gas heat exchanger B and heated to 270°C and introduced into the reactor C.

The amount of distillation column D column top gas bypassing the intermediate heat exchanger C' of the reactor C was controlled to set the temperature of the reactor exit gas to 320°C, and when the reactor exit gas had passed through the gas/gas heat exchanger B the gas temperature was 236°C. This was then passed through the evaporator A where the temperature fell to 130°C, and at this stage some of the gas had been liquefied.

The gas/liquid mixture emerging from the evaporator A was introduced as it was into the reboiler of distillation column G. The column bottom pressure of distillation column G was 5.0 kg/cm<sup>2</sup>(G) and the contents of the reboiler H boiled at

60°C. The reaction product temperature fell to 105°C at this point and it was introduced into distillation column D. The column top pressure of distillation column D was maintained at 17 kg/cm<sup>2</sup>(G) and the column top gas and some of the reflux liquid was recycled to the reaction system. The column bottom liquid of distillation column D was obtained at a rate of 2690 kg/h (5.0% monomethylamine, 42.7% dimethylamine, 3.8% trimethylamine, 8.0% methanol, 40.5% water) and this was passed sequentially through distillation columns E → F → G and monomethylamine, dimethylamine and trimethylamine were obtained as the respective products.

In the process described above the aim could be achieved without using steam for heating purposes in the evaporator A and the reboiler H. The consequent reduction in the amount of steam for heating purposes achieved was 2.5 T/h. Furthermore, throughout this process the amount of steam heating employed was about half of that used when a conventional catalyst was being used.

#### **4. Brief Explanation of the Drawing**

The drawing is a flow sheet showing the reaction process of the present invention.

A: Ammonia, methanol evaporator

B: Heat exchanger

C: Reaction column, C': Intermediate heat exchanger

D: Ammonia separating column

E: Trimethylamine separating column

F: Water, methanol separating column

G: Monomethylamine/diethylamine separating column

H: Reboiler

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